Electroneutrality and Phase Behavior of Colloidal Suspensions

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Several statistical mechanical theories predict that colloidal suspensions of highly charged macroions and monovalent microions can exhibit unusual thermodynamic phase behavior when strongly deionized. Density-functional, extended Debye-Hückel, and response theories, within mean-field and linearization approximations, predict a spinodal phase instability of charged colloids below a critical salt concentration. Poisson-Boltzmann cell model studies of suspensions in Donnan equilibrium with a salt reservoir demonstrate that effective interactions and osmotic pressures predicted by such theories can be sensitive to the choice of reference system, e.g., whether the microion density profiles are expanded about the average potential of the suspension or about the reservoir potential. By unifying Poisson-Boltzmann and response theories within a common perturbative framework, it is shown here that the choice of reference system is dictated by the constraint of global electroneutrality. On this basis, bulk suspensions are best modeled by density-dependent effective interactions derived from a closed reference system in which the counterions are confined to the same volume as the macroions. Lower-dimensional systems (e.g., monolayers, clusters), depending on the strength of macroion-counterion correlations, may be governed instead by density-independent effective interactions tied to an open reference system with counterions dispersed throughout the reservoir, possibly explaining observed structural crossover in colloidal monolayers and anomalous metastability of colloidal crystallites.

I. INTRODUCTION

A variety of experiments have demonstrated the unusual thermodynamic properties of deionized charge-stabilized colloidal suspensions [1]. Aqueous suspensions of highly charged macroions and monovalent microions at sub-millimolar ionic strengths reportedly can display liquid-vapor coexistence [2], stable void structures [3–5], compressed crystals [5, 6], metastable crystallites [7], and macroion gathering near glass plates [7, 8]. Such phenomena have been interpreted by some workers [2–5] as evidence for pair attraction of like-charged macroions, in seeming defiance of the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) [9] and Poisson-Boltzmann (PB) [10] theories. Others have attributed anomalous behavior to nonequilibrium phenomena [11], polyelectrolyte impurities [12], and many-body effects [13]. While some molecular simulations of the primitive model display macroion aggregation [14–23], such computationally demanding methods are usually limited to size and charge asymmetries corresponding to relatively strongly correlated microions and weakly charged macroions.

Several common statistical mechanical theories, including density-functional [24–27], extended Debye-Hückel [28–30], and response [31–35] theories, predict similarly surprising thermodynamic phase behavior of deionized suspensions [36]. Such coarse-grained theories preaverage the microion degrees of freedom, reducing the ion mixture to an effective one-component model. Most practical implementations assume a mean-field approximation for the microion structure, which neglects microion correlations; some form of linearization approximation, which ignores nonlinear screening of macroions by microions; and a fixed (state-independent) effective macroion charge. Under these assumptions, the various approaches reduce to variants of linearized PB theory, all predicting a screened-Coulomb (Yukawa) effective pair potential and a one-body volume energy. Although independent of macroion coordinates, the volume energy contributes density-dependent terms to the total free energy that can drive a spinodal instability of highly charged suspensions below a critical salt concentration [24–28, 35]. Such unusual phase behavior occurs, however, at parameters as yet inaccessible to primitive model simulations and may be qualitatively modified by ion correlations and nonlinear screening.

Recent studies of colloidal suspensions in Donnan equilibrium [37, 38] with an electrolyte reservoir demonstrate that predictions of linearized PB theory can be sensitive to the choice of reference system [39–42]. While expansion of the microion densities about the average potential of the system leads to phase separation at low salt concentrations, expansion about the reservoir potential strictly predicts phase stability, in qualitative agreement with nonlinear PB theory [39–43]. These studies suggest that the predicted phase separation may be merely a spurious artifact of linearization approximations.

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Although nonlinear PB theory is often presumed superior to its linearized form and, by implication, to related linearized theories, it is well to remember that mean-field theories do not faithfully model nonlinear screening near highly charged macroions, where counterions are strongly correlated. Indeed, strong counterion association can renormalize the effective macroion charge [44–50], modifying interparticle interactions and thermodynamic properties. Furthermore, nonlinear PB theory is computationally practical only within cell models [51], which require computing the microion distribution around just a single macroion, but thereby completely neglect macroion correlations. In contrast, linearized theories predict analytical expressions for effective interactions that are independent of any artificial cell geometry, become accurate sufficiently far from the macroions, and can be input into separate theories or simulations that incorporate ion correlations and charge renormalization. Linearized theories thus may play a vital role in multiscale approaches to modeling charged colloids.

The main purpose of this work is to carefully analyze implementations of linearization approximations in coarse-grained theories of charged colloids. Connections between PB and response theories are established and exploited to show that the constraint of global electroneutrality dictates the optimal choice of reference system. Theories linearized about a closed reference system, whose counterions are confined to the same volume as the macroions, are shown to predict density-dependent effective interactions and – assuming a fixed effective macroion charge – phase instability of deionized suspensions. In contrast, linearization about an open reference system, with counterions dispersed throughout the reservoir, predicts density-independent effective interactions and phase stability, but violates electroneutrality for bulk suspensions. Lower-dimensional suspensions (e.g., monolayers, clusters), on the other hand, may be modeled best – for sufficiently weak macroion-counterion correlations – by an open reference system, with important implications for thermodynamic properties.

The remainder of the paper is organized as follows. Section II first defines the primitive and effective one-component models. In Sec. III, effective electrostatic interactions and osmotic pressures are then derived from response theory and PB theory for closed and open reference systems. Corresponding predictions for the equation of state and phase diagram are presented and contrasted in Sec. IV. Section V closes with a summary and conclusions.

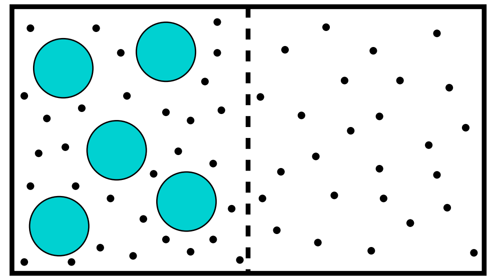

FIG. 1: Colloidal suspension (left) of macroions (larger circles) and microions (smaller circles) in Donnan equilibrium with a microion reservoir (right) via a semipermeable membrane (dashed line), which allows exchange only of microions.

II. MODELS

A. Primitive Model

We consider a charge-stabilized colloidal suspension in Donnan equilibrium [37, 38] with a microion reservoir (e.g., electrolyte). As depicted in Fig. 1, the suspension and reservoir are separated by a semipermeable membrane, which allows exchange of solvent and microions, but not macroions. The volumes of the suspension and reservoir are denoted by V and V_r, respectively. Within the primitive model of charged colloids [1], the solvent is modeled as a dielectric continuum, of dielectric constant ϵ, the macroions as N_m charged hard spheres, of radius a and effective valence Z (charge $-Ze$) and the microions as *monovalent* point charges, N_+ positive and N_- negative, totaling $N_\mu = N_+ + N_-$ in the suspension. It is assumed that all ions interact via only bare Coulomb and excluded-volume pair potentials and have the same dielectric constant as the solvent, justifying neglect of polarization effects.

The macroions have an average number density $n_m = N_m/V$, their hard cores occupying a volume fraction $\eta = (4\pi/3)n_m a^3$. The microions have average number densities $n_\pm = N_\pm/V'$ in the free volume $V' = V(1-\eta)$ outside the macroion cores. The reservoir is assumed to be a 1:1 symmetric electrolyte with number density of salt ion pairs n_r. Given Z counterions per macroion and N_s salt ion pairs, the ion numbers are related according to $N_+ = ZN_m + N_s$ and $N_- = N_s$ and the ion densities according to $n_+ = Zn_m/(1-\eta) + n_s$ and $n_- = n_s$, where $n_s = N_s/V'$ is the average salt density in the free volume. Overall electroneutrality of the suspension imposes the constraints $N_+ - N_- = ZN_m$ and $n_+ - n_- = Zn_m/(1-\eta)$.

B. Effective One-Component Model

By averaging over the microion degrees of freedom, the primitive model is mapped onto a one-component model of pseudomacroions, governed by effective interactions [52–56]. This coarse-graining procedure acts on the semigrand partition function $\langle\langle\exp(-\beta H)\rangle_\mu\rangle_m$, where $\langle\ \rangle_m$ denotes a canonical trace over macroion (m) coordinates, $\langle\ \rangle_\mu$ a grand canonical trace over microion (μ) coordinates, H is the Hamiltonian, and $\beta \equiv 1/k_BT$ at temperature T. Splitting H into macroion, microion, and macroion-microion interaction terms, according to $H = H_m + H_\mu + H_{m+} + H_{m-}$, and tracing over the microions yields the semigrand potential,

$$\Omega_{\rm sg} = -k_BT \ln\langle\exp(-\beta H_{\rm eff})\rangle_m, \tag{1}$$

where $H_{\rm eff} = H_m + \Omega_\mu$ is an effective one-component Hamiltonian and

$$\Omega_\mu = -k_BT \ln\left\langle\exp\left[-\beta(H_\mu + H_{m+} + H_{m-})\right]\right\rangle_\mu \tag{2}$$

is the grand potential of the microions amidst fixed macroions. Equations (1) and (2) provide a formal and exact foundation for both response theory (Sec. III A), which is based on a perturbative expansion of Ω_μ about a reference system, and PB theory (Sec. III B), which is based on a density-functional expansion of the grand potential functional.

III. THEORY

A. Linear-Response Theory

Response theory of charged colloids [31–35] views the electrostatic potential of the macroions as an "external" potential that *perturbs* the microions, inducing structure in their (otherwise uniform) density profiles. Within this view, the microion grand potential [Eq. (1)] can be expressed as

$$\Omega_\mu = \Omega_0 + \int_0^1 {\rm d}\lambda\ \left(\langle H_{m+}\rangle_\lambda + \langle H_{m-}\rangle_\lambda\right), \tag{3}$$

where $\Omega_0 = -k_BT \ln\left\langle\exp(-\beta H_\mu)\right\rangle_\mu$ is the grand potential of a reference system in which the macroions are uncharged and the microions are unperturbed, λ is a charging parameter, and $\langle\ \rangle_\lambda$ represents a grand canonical ensemble average for macroion valence λZ. In practice, it proves convenient to add to and subtract from Ω_0 the energy E_b of a uniform, neutralizing background, having charge density opposite that of the unperturbed microions, and to define $\Omega_p = \Omega_0 + E_b$ as the grand potential of a uniform (electroneutral) reference microion plasma.

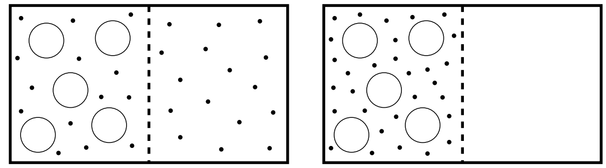

FIG. 2: Open (left) and closed (right) reference systems in linear-response theory of a salt-free colloidal suspension. Larger circles represent uncharged (hard-sphere) colloids and smaller circles charged counterions.

For a sealed suspension whose macroions and microions share the same volume, the reference system is unambiguous. For a suspension in Donnan equilibrium, however, two choices seem to be possible:
(1) A "closed" reference system, in which the counterions are confined, with the macroions, to the suspension. Independent of reservoir size, the microion densities in the reference system are then equal to those in the suspension.
(2) An "open" reference system, in which the microions are uniformly distributed throughout the combined volume of the system and the reservoir. In the limit of an infinite reservoir ($V_r/V \to \infty$), the microion densities in the reference system equal those in the reservoir.
The two choices are depicted in Fig. 2 in the idealized case of zero salt concentration. The second choice may seem most natural, since in the presence of neutral macroions the counterions would diffuse throughout the available volume to maximize entropy. On the other hand, in the real system (with charged macroions), electroneutrality confines the counterions to the suspension. Does it matter which reference system is adopted? By considering each case in turn, it is shown below that the choice matters, in practice, only for strongly deionized suspensions, but that the optimal choice then may depend on system dimensionality.

Linear-response theory [31–35] is first reviewed, emphasizing the role of the reference system. The external potential at position $\mathbf{r}$ is defined as

$$v_{\rm ext}(\mathbf{r}) = \int_{V'} {\rm d}\mathbf{r}'\, v_{m\pm}(|\mathbf{r}-\mathbf{r}'|) n_m(\mathbf{r}'), \tag{4}$$

where $v_{m\pm}(r) = Ze^2/\epsilon r$ $(r > a)$ are the macroion-microion Coulomb pair potentials and $n_m(\mathbf{r})$ is the macroion density. The macroion-microion interactions then can be expressed as

$$\begin{aligned} H_{m\pm} &= \int_{V'} {\rm d}\mathbf{r}\, v_{\rm ext}(\mathbf{r}) n_\pm(\mathbf{r}) \\ &= \frac{1}{V'}\sum_{\mathbf{k}} \hat{v}_{m\pm}(k)\hat{n}_m(\mathbf{k})\hat{n}_\pm(-\mathbf{k}), \end{aligned} \tag{5}$$

where $n_\pm(\mathbf{r})$ denote the microion density profiles and the Fourier transform is defined according to $\hat{n}_m(\mathbf{k}) = \int_{V'} d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r}) n_m(\mathbf{r})$, with inverse $n_m(\mathbf{r}) = (1/V')\sum_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})\hat{n}_m(\mathbf{k})$.

Expanding $n_\pm(\mathbf{r})$ in a functional Taylor series in powers of $v_{\rm ext}(\mathbf{r})$ yields [33]

$$\hat{n}_\pm(\mathbf{k}) = \chi_\pm(k)\hat{v}_{m\pm}(k)\hat{n}_m(\mathbf{k}) + \cdots, \quad k \neq 0, \quad (6)$$

where $\chi_\pm(k)$ are (partial) linear-response functions, associated with the microion structure in the reference system, higher-order terms involve nonlinear response functions and higher powers of the macroion density [34, 35], and the zero-wavevector (long-wavelength) component is fixed by the normalization condition $\hat{n}_\pm(0) = N_\pm$. Combining Eqs. (3), (5), and (6), the effective Hamiltonian can be written as [32–34]

$$H_{\rm eff} = H_{\rm HS} + E + \frac{1}{2}\sum_{i\neq j=1}^{N_m} v_{\rm eff}(r_{ij}) + \cdots, \quad (7)$$

where $H_{\rm HS}$ is the hard-sphere (HS) Hamiltonian associated with the macroion cores, E is a one-body volume energy, $v_{\rm eff}(r)$ is an effective electrostatic pair potential between macroions whose centers are separated by r, and higher-order terms involve effective many-body interactions [34, 57, 58]. The effective pair potential,

$$v_{\rm eff}(r) = v_{mm}(r) + v_{\rm ind}(r) \quad (8)$$

is the sum of the bare macroion-macroion Coulomb pair potential $v_{mm}(r) = Z^2e^2/\epsilon r$ and a microion-induced pair potential $v_{\rm ind}(r)$. Within a linear-response approximation [33],

$$\hat{v}_{\rm ind}(k) = \chi(k)[\hat{v}_{m+}(k)]^2, \quad (9)$$

where $\chi(k) \equiv \chi_+(k) + \chi_-(k)$ is the (total) linear-response function. Equations (7)-(9) are general expressions for the effective interactions. More explicit expressions depend on the specific reference system.

In a *closed* reference system, where the unperturbed microions have average densities $n_\pm$, a simple ideal-gas approximation yields

$$\beta\Omega_p = N_+\left[\ln\left(\frac{n_+}{n_r}\right) - 1\right] + N_-\left[\ln\left(\frac{n_-}{n_r}\right) - 1\right], \quad (10)$$

assuming weakly correlated microions with (electro)chemical potentials [59] fixed by the reservoir: $\mu_\pm = \mu_r = k_BT\ln(n_r\Lambda^3)$, Λ being the microion thermal wavelength. The one-body volume energy is given by [33]

$$\begin{aligned} E &= \Omega_p + \frac{N_m}{2}v_{\rm ind}(0) + N_m(n_+ - n_-) \\ &\times \lim_{k\to 0}\left[\hat{v}_{m+}(k) - \frac{1}{2Z}\hat{v}_{\rm ind}(k) + \frac{Z}{2}\hat{v}(k)\right], \end{aligned} \quad (11)$$

where $\hat{v}(k)$ is the Fourier transform of the counterion-counterion Coulomb pair potential $v(r) = e^2/\epsilon r$. The linear-response functions are related to the static structure factor $S(k)$ of the closed reference microion plasma [60] via

$$\chi_\pm(k) = \mp\beta n_\pm S(k) = \mp\frac{\beta n_\pm}{1 - n_\mu\hat{c}(k)}, \quad (12)$$

where $n_\mu = n_+ + n_- = Zn_m/(1-\eta) + 2n_s$ is the total average microion density in the free volume of the suspension and $\hat{c}(k)$ is the Fourier transform of the counterion-counterion direct correlation function. Within a random-phase approximation [60] for the microion structure, which neglects all but asymptotically long-ranged microion correlations, $\hat{c}(k) = -\beta\hat{v}(k)$ and the linear-response functions become

$$\chi_\pm(k) = \mp\frac{\beta n_\pm}{1 + \kappa^2/k^2}, \quad (13)$$

where $\kappa = \sqrt{4\pi n_\mu\lambda_B}$ is the Debye screening constant and $\lambda_B = \beta e^2/\epsilon$ is the Bjerrum length. Taking into account exclusion of the microions from the macroion cores leads to macroion-microion potentials of the form [33]

$$\hat{v}_{m\pm}(k) = \mp\frac{4\pi Ze^2}{\epsilon(1+\kappa a)k^2}\left[\cos(ka) + \kappa\frac{\sin(ka)}{k}\right]. \quad (14)$$

Substituting Eqs. (13) and (14) into Eqs. (9) and (11) results in explicit analytical expressions for the effective interactions, namely a screened-Coulomb (Yukawa) effective pair potential [33]

$$v_{\rm eff}(r) = \frac{Z^2e^2}{\epsilon}\left(\frac{e^{\kappa a}}{1+\kappa a}\right)^2\frac{e^{-\kappa r}}{r}, \qquad r \geq 2a \quad (15)$$

and a volume energy

$$\beta E = \beta\Omega_p - \frac{N_mZ^2}{2}\frac{\kappa\lambda_B}{1+\kappa a} - \frac{N_mZ}{2}\frac{n_+ - n_-}{n_\mu}, \quad (16)$$

whose three terms incorporate, respectively, the microion entropy, the macroion self-energy, and the average microion potential energy. The latter term is a direct manifestation of the Donnan effect [37, 38] – the unequal distribution of microions between the suspension and reservoir resulting from the impermeability of the interface to the macroions. Diffusion of counterions from the suspension into the reservoir generates an interfacial charge and a resultant electric field that pulls the counterions back to maintain global electroneutrality of the suspension. The electrostatic potential of the suspension is

thereby shifted, by the Donnan potential Ψ_D, relative to that of the reservoir to equalize the microion chemical potentials. In terms of Ψ_D, the final term in Eq. (16) can be expressed as $(n_+ - n_-)e\Psi_D/2$, which is simply the work required to move microions from the reservoir (at zero potential) to the suspension (at potential Ψ_D).

It is vital to note that the effective pair potential [Eq. (15)] and volume energy [Eq. (16)] derived from the closed reference system depend implicitly (via κ) on the average microion densities in the suspension. The electroneutrality constraint then imposes a dependence of $v_{\rm eff}(r)$ and E on the macroion density. As discussed below in Sec. IV, this density dependence entails an effective many-body cohesion that can profoundly impact the bulk phase behavior of counterion-dominated suspensions.

In an *open* reference system, the unperturbed microions are not confined with the macroions, but instead uniformly fill the combined free volume of the suspension and reservoir. The effective interactions are now still described by Eqs. (15) and (16), but with the average microion densities in the suspension $n_\pm$ replaced by the average microion densities in the suspension + reservoir, i.e., $(n_\pm + n_r V_r/V')/(1 + V_r/V')$. In the limit of an infinite reservoir ($V_r/V' \to \infty$), the reference microion densities approach n_r and the reference microion plasma grand potential [Eq. (10)] $\beta\Omega_p \to -2n_r V'$. In this same limit, the linear-response functions, now associated with the microion structure of the reservoir, become [cf. Eq. (13)]

$$\chi_\pm^{(r)}(k) = \mp \frac{\beta n_r}{1 + \kappa_r^2/k^2}, \qquad (17)$$

where $\kappa_r = \sqrt{8\pi n_r \lambda_B}$ is the *reservoir* screening constant. Likewise, the effective pair potential retains the Yukawa form [Eq. (15)] with κ replaced by κ_r and the volume energy reduces to [cf. Eq. (16)]

$$\beta E_r = -2n_r V' - \frac{N_m Z^2}{2}\frac{\kappa_r \lambda_B}{1 + \kappa_r a}. \qquad (18)$$

Note that the electroneutrality term [final term of Eq. (16)] vanishes, since in the infinite-reservoir limit the reference microion plasma contains equal densities of positive and negative microions, the counterions having "evaporated" into the reservoir.

Thus, when applied to a suspension in Donnan equilibrium with a microion reservoir, linear-response theory predicts nontrivial dependence of the effective interactions on macroion density only when the effective Hamiltonian is perturbed about a closed reference system. If the perturbative expansion is performed about an open reference system, the volume energy – in the case of an infinite reservoir – is independent of macroion density and hence does not influence thermodynamics. Clearly the distinction between reference systems can have practical relevance only if the counterion concentration is not overwhelmed by the salt ion concentration. Section IV identifies a physical criterion for selecting the optimal reference system and explores implications for phase stability of deionized suspensions.

B. Linearized Poisson-Boltzmann Theory

An alternative, and widely studied, approach to modeling charged colloidal suspensions and polyelectrolyte solutions is the Poisson-Boltzmann theory, here briefly reviewed with emphasis on connections to response theory and the role of the reference system. Poisson-Boltzmann theory can be derived from the microion grand potential [61]

$$\Omega_\mu[n_+(\mathbf{r}), n_-(\mathbf{r})] = \mathcal{F}_\mu - \mu_+ N_+ - \mu_- N_-, \qquad (19)$$

regarded as a functional of the nonuniform microion number densities $n_\pm(\mathbf{r})$ in the external potential $v_{\rm ext}(\mathbf{r})$ of the macroions [Eq. (4)]. The microion Helmholtz free energy functional separates naturally, according to

$$\mathcal{F}_\mu[n_+(\mathbf{r}), n_-(\mathbf{r})] = \mathcal{F}_{\rm id} + \mathcal{F}_{\rm ext} + \mathcal{F}_{\rm ex}, \qquad (20)$$

into an ideal-gas free energy

$$\begin{aligned} \mathcal{F}_{\rm id} &= k_B T \int_{V'} d\mathbf{r}\, \big(n_+(\mathbf{r})\{\ln[n_+(\mathbf{r})\Lambda^3] - 1\} \\ &+ n_-(\mathbf{r})\{\ln[n_-(\mathbf{r})\Lambda^3] - 1\}\big), \end{aligned} \qquad (21)$$

due to the microion entropy, an external free energy

$$\mathcal{F}_{\rm ext} = \int_{V'} d\mathbf{r}\, v_{\rm ext}(\mathbf{r})[n_+(\mathbf{r}) - n_-(\mathbf{r})], \qquad (22)$$

associated with microion-macroion interactions, and an excess free energy $\mathcal{F}_{\rm ex}$, due to microion-microion interactions. In a mean-field (Hartree) approximation, which neglects all interparticle correlations, the excess free energy can be written as

$$\begin{aligned} \mathcal{F}_{\rm ex} &= \frac{1}{2}\int_{V'} d\mathbf{r} \int_{V'} d\mathbf{r}'\, v(|\mathbf{r} - \mathbf{r}'|)[n_+(\mathbf{r}) - n_-(\mathbf{r})] \\ &\times\ [n_+(\mathbf{r}') - n_-(\mathbf{r}')]. \end{aligned} \qquad (23)$$

Combining Eqs. (19)-(23) and minimizing $\Omega_\mu[n_+(\mathbf{r}), n_-(\mathbf{r})]$ with respect to $n_\pm(\mathbf{r})$, for a given macroion density, leads to Boltzmann distributions for the equilibrium microion densities:

$$n_\pm(\mathbf{r}) = n_r \exp[\mp\beta e\Psi(\mathbf{r})], \qquad (24)$$

where the electrostatic potential $\Psi(\mathbf{r})$ is defined via

$$e\Psi(\mathbf{r}) = \int_{V'} \mathrm{d}\mathbf{r}'\, v(|\mathbf{r}-\mathbf{r}'|)n(\mathbf{r}'), \tag{25}$$

with $n(\mathbf{r}) \equiv n_+(\mathbf{r}) - n_-(\mathbf{r}) - n_f(\mathbf{r})$ the total number density of all charges, including those fixed on the macroion surfaces $n_f(\mathbf{r})$. Equation (24) and the exact Poisson equation

$$\nabla^2\Psi(\mathbf{r}) = -\frac{4\pi e}{\epsilon}n(\mathbf{r}) \tag{26}$$

together determine $\Psi(\mathbf{r})$ and $n_\pm(\mathbf{r})$ under prescribed boundary conditions. The total free energy functional (for fixed macroions), $\mathcal{F} = E_{mm} + \mathcal{F}_\mu$, which includes the macroion-macroion Coulomb interaction energy, $E_{mm} = \sum_{i<j} v_{mm}(r_{ij})$, is given by

$$\mathcal{F} = \mathcal{F}_{\mathrm{id}} + \frac{e}{2}\int_{V'} \mathrm{d}\mathbf{r}\, \Psi(\mathbf{r})n(\mathbf{r}) \tag{27}$$

or, within a cell model approximation,

$$\mathcal{F} = \mathcal{F}_{\mathrm{id}} + N_m\frac{\epsilon}{8\pi}\int_{\mathrm{cell}} \mathrm{d}\mathbf{r}\, |\nabla\Psi(\mathbf{r})|^2, \tag{28}$$

using Eq. (26) and assuming vanishing electric field ($\nabla\Psi = 0$) at the cell boundary.

More generally, independent of any cell geometry, and for any fixed macroion distribution, the microion free energy functional can be expressed as

$$\mathcal{F}_\mu = \mathcal{F}_{\mathrm{id}} + \frac{1}{V'}\sum_{\mathbf{k}} \hat{v}_{m+}(k)\hat{n}_m(\mathbf{k})[\hat{n}_+(-\mathbf{k}) - \hat{n}_-(-\mathbf{k})] + \frac{1}{2V'}\sum_{\mathbf{k}} \hat{v}(k)[\hat{n}_+(\mathbf{k}) - \hat{n}_-(\mathbf{k})][\hat{n}_+(-\mathbf{k}) - \hat{n}_-(-\mathbf{k})]. \tag{29}$$

A systematic scheme for further approximations is based on expansion of the microion density profiles [Eq. (24)] about a reference potential Ψ_0 and a functional Taylor-series expansion of the ideal-gas free energy [Eq. (21)] about reference densities $n_\pm^{(0)}$. In linearized PB theory, the expansions of $n_\pm(\mathbf{r})$ are truncated at linear order in the potential deviation,

$$n_\pm(\mathbf{r}) = n_\pm^{(0)}\{1 \mp \beta e[\Psi(\mathbf{r}) - \Psi_0]\}, \tag{30}$$

and the expansion of $\mathcal{F}_{\mathrm{id}}$ is truncated at quadratic order in the density deviations,

$$\mathcal{F}_{\mathrm{id}} = k_BT\sum_{i=\pm}\left\{N_i \ln\left(n_i^{(0)}\Lambda^3\right) - V'n_i^{(0)} + \frac{1}{2n_i^{(0)}}\int_{V'} \mathrm{d}\mathbf{r}\, \left[n_i(\mathbf{r}) - n_i^{(0)}\right]^2\right\}, \tag{31}$$

where $n_\pm^{(0)} \equiv n_r \exp(\mp\beta e\Psi_0)$ are the reference microion densities. Analogous to the choice in linear-response theory between closed and open reference systems, here two choices of reference potential and corresponding microion densities are apparent:

(1) The average potential and microion densities in the suspension, $\Psi_0 = \overline{\Psi}$ and $n_\pm^{(0)} = n_\pm$.

(2) The average potential and microion densities in the reservoir, $\Psi_0 = 0$ and $n_\pm^{(0)} = n_r$.

Although the second choice is most commonly assumed, the first has been advocated [39–41] as better exploiting the supposedly weak deviations, $[\Psi(\mathbf{r}) - \overline{\Psi}]$ and $[n_\pm(\mathbf{r}) - n_\pm]$.

Expanding $n_\pm(\mathbf{r})$ first about $\Psi_0 = \overline{\Psi}$, and combining the Fourier transform of the linearized expansion with that of Eq. (25),

$$e\hat{\Psi}(\mathbf{k}) = \hat{v}_{m+}(k)\hat{n}_m(\mathbf{k}) + \hat{v}(k)[\hat{n}_+(\mathbf{k}) - \hat{n}_-(\mathbf{k})], \tag{32}$$

the microion densities take on the form

$$\hat{n}_\pm(\mathbf{k}) = \mp n_\pm\beta e\hat{\Psi}(\mathbf{k}) = \chi_\pm(k)\hat{v}_{m\pm}(k)\hat{n}_m(\mathbf{k}), \quad k \neq 0, \tag{33}$$

where $\chi_\pm(k)$ are identical to the linear-response functions that appear in Eqs. (6) and (13). Equation (33) implies that

$$\hat{n}_+(\mathbf{k}) - \hat{n}_-(\mathbf{k}) = \chi(k)\hat{v}_{m+}(k)\hat{n}_m(\mathbf{k}), \qquad k \neq 0. \tag{34}$$

From the inverse transform of Eq. (33), using Eqs. (13) and (14), the electrostatic potential around an isolated macroion is then given by

$$\Psi(r) = -\frac{Ze}{\epsilon}\frac{e^{\kappa a}}{1+\kappa a}\frac{e^{-\kappa r}}{r}, \qquad r \geq a, \tag{35}$$

which is identical to the solution of the Poisson equation [Eq. (26)] with boundary conditions $\Psi'(r)|_{r=a} = -Ze/\epsilon a^2$ and $\Psi(r) \to 0$ as $r \to \infty$. The corresponding expansion of $\mathcal{F}_{\mathrm{id}}$ about the average microion densities becomes

$$\mathcal{F}_{\mathrm{id}} = k_BT\sum_{i=\pm}\left\{N_i[\ln(n_i\Lambda^3) - 1] + \frac{1}{2n_iV'}\sum_{\mathbf{k}\neq 0}\hat{n}_i(\mathbf{k})\hat{n}_i(-\mathbf{k})\right\}, \tag{36}$$

where the $k = 0$ term vanishes via normalization: $\int_{V'} \mathrm{d}\mathbf{r}\, n_\pm(\mathbf{r}) = n_\pm V'$. Combining Eqs. (29), (33), and (36) then yields the microion Helmholtz free energy (equilibrium value of $\mathcal{F}_\mu$) for fixed macroions,

$$
\begin{aligned}
F_\mu &= k_BT\sum_{i=\pm} N_i[\ln(n_i\Lambda^3)-1] \\
&+ \frac{1}{2V'}\sum_{\mathbf{k}\neq 0}\hat{v}_{\rm ind}(k)\hat{n}_m(\mathbf{k})\hat{n}_m(-\mathbf{k}) + (n_+ - n_-) \\
&\times \lim_{k\to 0}\left[\frac{1}{2}(N_+ - N_-)\hat{v}(k) + N_m\hat{v}_{m+}(k)\right], \quad (37)
\end{aligned}
$$

the $k = 0$ terms being determined by the electroneutrality constraint. Significantly, this free energy generates *precisely* the same effective Hamiltonian, $H_{\rm eff} = H_{\rm HS} + F - N_\mu\mu_r$, as derived above (Sec. III A) from response theory perturbed about a closed reference system [Eqs. (7)-(11)].

Expanding $n_\pm(\mathbf{r})$ now about the reservoir potential ($\Psi_0 = 0$), the Fourier transform of the linearized microion densities combined with Eq. (32) yields

$$
\hat{n}_\pm(\mathbf{k}) = \mp n_r\beta e\hat{\Psi}(\mathbf{k}) = \chi_\pm^{(r)}(k)\hat{v}_{m\pm}^{(r)}(k)\hat{n}_m(\mathbf{k}), \quad k\neq 0, \quad (38)
$$

from which

$$
\hat{n}_+(\mathbf{k}) - \hat{n}_-(\mathbf{k}) = \chi^{(r)}(k)\hat{v}_{m+}^{(r)}(k)\hat{n}_m(\mathbf{k}), \qquad k\neq 0, \quad (39)
$$

where $\chi_\pm^{(r)}(k)$ are the linear-response functions of Eq. (17), $\chi^{(r)}(k) \equiv \chi_+^{(r)}(k) - \chi_-^{(r)}(k)$, and $\hat{v}_{m\pm}^{(r)}(k)$ are given by Eq. (14), with κ replaced by κ_r. The expansion of $\mathcal{F}_{\rm id}$ about the reservoir microion density becomes

$$
\begin{aligned}
\beta\mathcal{F}_{\rm id} &= N_\mu[\ln(n_r\Lambda^3)-1] - n_rV' \\
&+ \frac{1}{2n_rV'}\sum_{i=\pm}\sum_{\mathbf{k}}\hat{n}_i(\mathbf{k})\hat{n}_i(-\mathbf{k}), \quad (40)
\end{aligned}
$$

the $k = 0$ term now nonvanishing. Substituting Eqs. (38)-(40) into Eq. (29) then yields

$$
\begin{aligned}
\beta F_\mu &= N_\mu[\ln(n_r\Lambda^3)-1] - n_rV' + \frac{(N_+ + N_-)^2}{4n_rV'} \\
&+ \frac{\beta}{2V'}\sum_{\mathbf{k}}\hat{v}_{\rm ind}^{(r)}(k)\hat{n}_m(\mathbf{k})\hat{n}_m(-\mathbf{k}), \quad (41)
\end{aligned}
$$

where $\hat{v}_{\rm ind}^{(r)}(k) \equiv \chi^{(r)}(k)[\hat{v}_{m+}^{(r)}(k)]^2$ is an induced potential that depends (via κ_r) on only the reservoir microion density n_r. This free energy corresponds to essentially the same effective Hamiltonian as derived from response theory perturbed about the open (reservoir) reference system, including the same effective pair potential [Eq. (15) with reservoir screening constant κ_r], but a slightly different volume energy [cf. Eq. (18)],

$$
\beta E_r = V'\left(\frac{n_\mu^2}{4n_r} - n_\mu - n_r\right) - \frac{N_mZ^2}{2}\frac{\kappa_r\lambda_B}{1+\kappa_r a}. \quad (42)
$$

Two main conclusions follow from the above derivations. First, linearization about the average potential and microion densities of the suspension leads to effective interactions that depend on macroion density, while linearization about the reservoir yields density-independent interactions. Second, linear-response and linearized PB theories are formally equivalent [62], with direct correspondences between closed/open and suspension/reservoir reference systems. In Sec. IV, these connections are exploited to bolster previous arguments [39–42] for linearizing PB theory about the average potential of the suspension, rather than that of the reservoir.

C. Thermodynamic Properties

Despite the presence of three ion species in the real suspension, thermodynamic properties of the effective one-component model depend on the chemical potentials of only pseudomacroions μ_m and salt ion pairs μ_s, since electroneutrality permits exchange of ions only in electroneutral units. A suspension in Donnan equilibrium with a salt reservoir, at fixed salt chemical potential $\mu_s = 2\mu_r = 2k_BT\ln(n_r\Lambda^3)$, has a total pressure $p = n_m\mu_m - \omega$ and a pseudomacroion chemical potential $\mu_m = (\partial\omega/\partial n_m)_{\mu_s}$, where $\omega \equiv \Omega/V$. The semigrand potential density of the suspension can be expressed as

$$
\omega(n_m, \mu_s) = f_{\rm eff} + \varepsilon, \quad (43)
$$

where $f_{\rm eff}$ is the free energy density of the one-component system interacting via the Yukawa effective pair potential [Eq. (15)], with screening constant κ or κ_r, and $\varepsilon = E/V$ [Eq. (16)] or E_r/V [Eq. (18)] for closed or open reference systems, respectively. The salt density in the suspension is determined by solving for n_s the implicit relation $\mu_s = (\partial f/\partial n_s)_{n_m}$, where

$$
f(n_m, n_s) = \omega + \mu_s n_s \quad (44)
$$

is the total free energy density of the suspension [63].

The dependence of effective interactions on the choice of reference system has important implications for the osmotic pressure of deionized suspensions. Substituting the appropriate volume energies into Eq. (43) yields, for the closed reference system,

$$
\beta p = n_\mu + n_m + \beta p_{\rm ex}(n_\mu) - \frac{Z(n_+ - n_-)\kappa\lambda_B}{4(1+\kappa a)^2}, \quad (45)
$$

and for the open reference system and an infinite reservoir,

$$
\beta p = 2n_r + n_m + \beta p_{\rm ex}(n_r), \quad (46)
$$

where

$$p_{\rm ex} = n_m \left(\frac{\partial f_{\rm ex}}{\partial n_m}\right)_{N_s/N_m} - f_{\rm ex} \qquad (47)$$

is the excess pressure due to effective macroion-macroion pair interactions (with respective screening constant κ or κ_r) and $f_{\rm ex} = F_{\rm ex}/V$ is the excess free energy density. The first two terms on the right sides of Eqs. (45) and (46) are the pressure contributions from microion and macroion translational entropy. The final term in Eq. (45), notably absent from Eq. (46), results from the density dependence of the microion-macroion interactions and thus is a manifestation of electroneutrality. For the open reference system and a finite reservoir, Eq. (45) applies with the simple reassignment $n_\pm \to (n_\pm + n_r V_r/V')/(1 + V_r/V')$, i.e., average microion densities in suspension + reservoir.

The excess free energy density can be accurately approximated by a variational method [24–26, 35] based on first-order thermodynamic perturbation theory with a hard-sphere reference system [60]:

$$f_{\rm ex}(n_m, n_s) = \min_{(d)} \left\{ f_{\rm HS}(n_m, n_s; d) + 2\pi n_m^2 \right.$$
$$\left. \times \int_d^\infty {\rm d}r\, r^2 g_{\rm HS}(r, n_m; d) v_{\rm eff}(r, n_m, n_s) \right\}, \qquad (48)$$

where the effective hard-sphere diameter d is the variational parameter and $f_{\rm HS}(n_m, n_s; d)$ and $g_{\rm HS}(r, n_m; d)$ are the excess free energy density and (radial) pair distribution function, respectively, of the HS fluid, computed here from the essentially exact Carnahan-Starling and Verlet-Weis expressions [60]. From the Gibbs-Bogoliubov inequality [60], minimization with respect to d generates a least upper bound to the free energy.

The phase diagram can be computed from a (Maxwell) common-tangent construction on the curve of ω vs n_m at fixed salt chemical potential, which imposes equality of the pressure and of the chemical potentials of macroions and salt in coexisting phases. As an internal consistency check, it is possible also to calculate the chemical potentials of the individual microion species, $\mu_\pm = (\partial F/\partial N_\pm)_{V,N_m,N_\mp}$. Chemical equilibrium between the suspension and reservoir requires

$$\beta(\mu_+ - \mu_-) = \ln\left(\frac{n_+}{n_-}\right) - 2\,\frac{n_+ - n_-}{n_\mu} = 0, \qquad (49)$$

which follows from Eq. (16) and symmetry of κ with respect to interchange of n_+ and n_-.

IV. RESULTS AND DISCUSSION

The importance of choosing an appropriate reference system in linearized theories becomes clear upon examining the osmotic pressure $\Pi = p - 2n_r k_B T$ – the difference between the suspension and reservoir pressures – at constant salt activity $z_s = \exp(\beta\mu_s)/\Lambda^3$, along with the corresponding phase behavior. Figure 3 shows sample predictions of linear-response theory, with both closed and open reference systems, for macroion radius $a = 50$ nm and fixed effective valence $Z = 500$. While the present theory neglects any influence of charge renormalization on Z, and thus on phase behavior, the results at least qualitatively illustrate the significance of the electroneutrality constraint for deionized suspensions.

Linearization about a closed reference system predicts, at sufficiently low salt activity, a van der Waals loop in the equation of state (Π vs η), i.e., a range of volume fractions over which the compressibility is negative, independent of reservoir size [solid curve of Fig. 3(a)]. This unusual spinodal instability, first discovered by van Roij *et al.* [24–26], implies separation into macroion-rich (liquid) and macroion-poor (vapor) bulk phases [67] within the binodal of the corresponding phase diagram [solid curve of Fig. 3(b)]. Close examination reveals the instability to be a many-body effect driven by the density dependence of both the macroion self-energy and the electroneutrality terms in the volume energy [last two terms of Eq. (16)].

Linearization about an open reference system predicts, in sharp contrast, a van der Waals loop that narrows, and a liquid-vapor binodal that shrinks, with increasing reservoir volume [dashed curves of Fig. 3]. For $V_r > V$, the loop closes entirely and the binodal collapses, the compressibility then being strictly positive at all salt concentrations, implying a single stable fluid phase. Such a trend would imply the unphysical possibility of influencing bulk phase behavior by controlling the exchange of microions between suspension and reservoir, i.e., simply adjusting chemical boundary conditions. The corresponding salt concentrations in the suspension c_s (inset to Fig. 3(a)) also show qualitatively distinct trends, decreasing or increasing with increasing η for closed or open reference systems, respectively. The fact that real salt concentrations are generally lower in the suspension than in the reservoir [65] indicates a further unphysical property of the open reference system.

Accuracy of the linearization approximation can be probed by self-consistency checks. First, the average linearized potential in the suspension can be

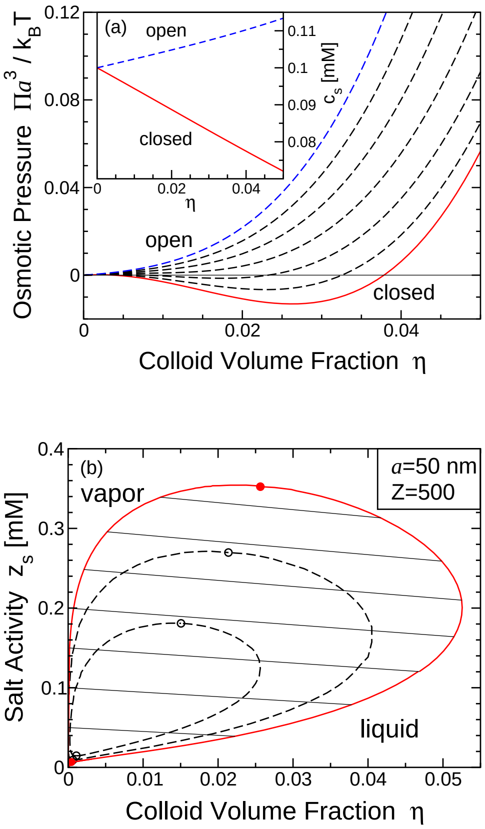

FIG. 3: Linear-response theory predictions for osmotic pressure (a) and phase diagram (b) of aqueous suspensions of macroions of diameter $a = 50$ nm and fixed effective valence $Z = 500$ in Donnan equilbrium with a 1:1 microion reservoir at salt activity $z_s = 0.1$ mM. Perturbation about closed reference system predicts phase instability [(a), solid curve] and vapor-liquid coexistence [(b), solid curve]. Perturbation about open reference system (dashed curves) predicts increased stability with increasing reservoir-to-suspension volume ratio $[V_r/V = 0, 0.2, 0.5, 1, 2, 5, \infty$, bottom to top in (a)] and, correspondingly, a shrinking binodal $[V_r/V = 0, 0.2, 0.5$, largest to smallest area in (b)]. Instability vanishes and binodal collapses for $V_r/V > 1$. Circles denote critical points and tie lines join coexisting phases. Inset of (a): salt concentration of suspension c_s with closed (solid) and open (dashed) reference systems for infinite reservoir ($V_r/V = \infty$).

estimated from Eq. (35):

$$\beta e|\overline{\Psi}| = 4\pi\beta e\frac{N_m}{V'}\int_a^\infty \mathrm{d}r\, r^2|\Psi(r)| = \frac{3}{(\kappa a)^2}\frac{Z\lambda_B}{a}\frac{\eta}{1-\eta}. \qquad (50)$$

For the electrostatic coupling considered here ($Z\lambda_B/a \simeq 7$), this estimate yields $\beta e|\overline{\Psi}| < 0.3$ along the binodal of Fig. 3(b). Although the potential is relatively high at the surface, $\beta e|\Psi(a)| \simeq 3$, it decays rapidly with distance from the surface. Integration of the microion density profiles [66] for these parameters shows that only 10-20% of the counterions are in the highly nonlinear region, $\beta e|\Psi(r) - \bar{\Psi}| > 1$, for salt activities $z_s > 0.05$ mM. By comparison, the artifacts of linearized PB theory demonstrated in Refs. [39–42] occur at much stronger couplings ($Z\lambda_B/a > 18$ and $\beta e|\overline{\Psi}| > 1$), where nonlinear effects are more significant. Second, when compared with (salt-free) primitive model simulations [18], linear-response theory [64] accurately predicts osmotic pressures for the same strength of electrostatic coupling, $Z\lambda_B/a = 7.1$ ($Z = 40, \lambda_B/a = 0.1779$). Third, the inclusion of first-order nonlinear terms in the effective interactions has been shown [35] for these parameters to only quantitatively alter the phase diagram, although higher-order nonlinear corrections may not necessarily be small. Fourth, the difference in chemical potentials between microion species [from Eq. (49)] is found to be negligible. Finally, a rigorous inequality involving the average microion densities in the suspension [41], $n_+n_- \geq n_r^2$, which follows from Eq. (24), is safely satisfied, as demonstrated in Fig. 4. Nevertheless, it is conceivable that charge renormalization could substantially modify the predicted phase behavior, even for such a relatively weak coupling.

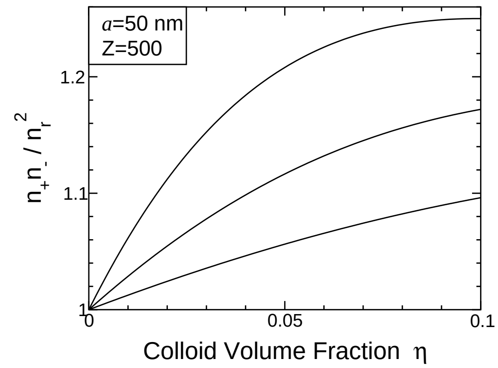

FIG. 4: Microion density inequality [41], $n_+n_- \geq n_r^2$, tested (and confirmed) at same parameters as Fig. 3 and salt activities $z_s = 0.1, 0.2, 0.4$ mM (top to bottom).

Returning to the choice of reference system, the common perturbative origin of linearized PB and response theories suggests a natural selection criterion. To minimize the magnitude of the perturbation term in the microion grand potential [Eq. (3)], and thereby optimize the accuracy of linearization, the reference system *alone* should reasonably describe the real suspension. On this basis, global electroneutrality clearly favors the closed over the open ref-

erence system for a bulk suspension. To appreciate why, consider that even monovalent macroions ($Z = 1$) would generate a macroscopic charge, which must be neutralized by a compensating counterion charge, lest the energy density diverge. Only a reference system whose counterions are confined to the same volume as the macroions, with a density hence slaved to the macroions, respects this constraint. Electroneutrality thus dictates the reference system of a bulk suspension and decouples phase behavior from boundary conditions.

A caveat to the above conclusions may be required in the case of Donnan equilibrium of lower-dimensional colloidal assemblies, e.g., monolayers (quasi-2D) or clusters (quasi-0D), whose ions are all near the surface and in direct contact with a reservoir. In such systems, electroneutrality does not necessarily constrain the majority of counterions to the volume occupied by the macroions. The distribution of counterions between the macroion region and the reservoir depends instead on the strength of macroion-counterion attraction and may determine whether a suspension is best modeled by an open or closed reference system.

For a colloidal monolayer (e.g., at an air-water interface or a glass surface), the range of counterion localization, compared with layer thickness, can be roughly quantified by estimating the Gouy-Chapman length l, i.e., the typical distance to which thermal energy can separate a counterion from the monolayer surface by working against electrostatic attraction of the macroions. Approximating a monolayer as a uniform surface charge density, and neglecting electrolyte screening, yields a lower limit of $l \simeq (\pi\alpha Z\lambda_B\rho)^{-1}$, where α is the fraction of escaped counterions and ρ is the areal density. In the dilute limit ($\rho a^2 \ll 1$), the Gouy-Chapman length can far exceed the monolayer thickness ($l \gg a$), implying weak localization of counterions by the macroions. In contrast, a suspension that is macroscopic in all three dimensions, *always* confines the vast majority of its counterions in bulk, considering that l is a microscopic length.

For a small cluster of macroions, a natural measure of counterion confinement is the escape energy, i.e., the energy required to remove a counterion from the cluster to the surrounding reservoir. An isolated, spherical cluster of N_m macroions with total charge $\alpha N_m Ze$ and volume fraction η binds a counterion near its surface with an escape energy $E_{\rm esc}$ that has an upper limit $\beta E_{\rm esc} \simeq \alpha(Z\lambda_B/a)N_m^{2/3}\eta^{1/3}$, again neglecting electrolyte screening. While counterions are tightly bound by large, densely charged clusters, they can escape from sufficiently small, dilutely charged clusters via thermal evaporation into the reservoir.

These considerations suggest that the effective interactions governing lower-dimensional colloidal assemblies may arise from a reference system dependent on particle number and charge density. A closed reference system – appropriate at high N_m, η, and Z – clearly entails density-dependent effective interactions and many-macroion cohesion in deionized suspensions. In contrast, an open reference system – appropriate at lower N_m, η, and Z, where the counterions are not enslaved by electroneutrality to the macroions – may yield density-independent effective interactions and pair repulsion of macroions.

Some support for this view comes from observations of quasi-2D monolayers in deionized aqueous suspensions [68–70]. In these experiments, highly charged PS particles were confined to a plane by light pressure and corralled via optical traps to effective surface charge densities of $\mathcal{O}(10^{-5})$ C/m^2 or $\mathcal{O}(10^{-4})$ e/nm^2. Effective pair potentials, obtained by inverting measured radial distribution functions, exhibited a density-independent Yukawa form at lower densities, crossing over to density-dependent non-Yukawa behavior at higher densities. These observations are consistent with salt-dominated linear screening in dilute monolayers, whose microion population is fixed by the reservoir, and nonlinear screening above a threshold macroion density. Colloidal monolayers confined between glass plates also reportedly can exhibit density-dependent effective pair interactions [71], although interpretation of such experiments is complicated by uncontrolled microion exchange with the glass surfaces.

Some evidence for size dependence in the stability of colloidal clusters comes from observations of metastable crystallites and macroion gathering in low-ionic-strength suspensions compressed near glass plates by external electric fields [7, 8]. Slow counterion evaporation from the macroions, and the associated crossover from cohesive many-body to repulsive pair effective interactions, might qualitatively explain the slow break-up of small macroion aggregates adrift in deionized water. For example, the fcc crystallites reported in Ref. [7] – characterized by $a = 326$ nm, $Z = 7300$, $\lambda_B = 0.72$ nm, $c_s < 5$ μM, and nearest-neighbor separations $d = 1.8$ μm – would correspond to $\beta E_{\rm esc} < 0.56\alpha N_m^{2/3}$. A crystallite of size $N_m = \mathcal{O}(10^2)$ could conceivably break up by gradually losing a substantial fraction of its counterions to the surrounding reservoir. Such a destabilization mechanism also could account for the observed increase in stability with increasing cluster size, without invoking any long-range pairwise attractive interaction. Although a crossover between closed and open reference systems appears consis-

tent with these experimental observations, a quantitative description requires further work.

V. CONCLUSIONS

Summarizing, this work analyzes the influence of the reference system on the effective electrostatic interactions and phase behavior predicted by linearized, coarse-grained theories of charged colloids. For a suspension in Donnan equilibrium with a microion reservoir, two reference systems are conceivable: one closed and the other open with respect to microion exchange with the reservoir. The constraint of global electroneutrality is shown to provide an objective physical basis for selecting between these two reference systems. From this criterion, and the unification of Poisson-Boltzmann and response theories, it is concluded that bulk suspensions are properly modeled within PB theory by expanding about the average potential and average microion densities within the suspension (*not* the reservoir), and within response theory by perturbing about a closed reference system, whose counterions share the same volume as the macroions.

Dependence of predictions on the reference system need not necessarily constitute a failing of linearized theories; it merely underscores the importance of correctly choosing the reference system. The optimal reference system identified in Ref. [41] for PB theory is the same one that respects electroneutrality in linear-response theory. The present conclusions thus broaden and clarify those of previous studies based on PB cell models [39–42]. When linearized about a physically consistent reference system, both PB and response theories predict a spinodal phase instability of highly deionized suspensions, assuming a state-independent effective macroion charge. Whether the predicted instability has any relevance to experimentally observed anomalies, however, can be decided only by resolving the important issues of nonlinear screening and charge renormalization.

Lower-dimensional systems – from monolayers to clusters – may be best described, depending on the strength of macroion-counterion correlations, by a closed reference system at high charge densities, but an open reference system at lower charge densities. The implied transition in effective interactions and thermodynamic properties may parallel an observed crossover, as a function of density, in the structure of colloidal monolayers and might qualitatively explain reports of metastable crystallites. Further comparisons with experiment are required to more fully evaluate these speculations. Future work should seek a more unified, cross-dimensional description of charged colloids. Generalization of the coarse-grained approach to richer models with multiple microion species – some exchanging with a reservoir and some trapped – may have applications to colloids or nanoparticles confined in pores and to proteins inside cells, where ion channels regulate exchange of ions across cell membranes.

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$$f_\pm(r) = x_\mp \frac{2\eta}{1-\eta}\left(\frac{r^3}{a^3}-1\right) \pm (x_+ - x_-) \times \left(1 - \frac{1+\kappa r}{1+\kappa a} e^{-\kappa(r-a)}\right), \quad r/a < 1/\eta^{1/3}.$$

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